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(54) Name of the invention: Fluorine containing compounds

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Patent Assignee: Kuraray Company

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[Note : Names, addresses, Company names and brand names are translated in the most common manner. Japanese Language does not have singular or plural words unless otherwise specified with numeral prefix or general form of plurality suffix. Translator's note.]

(54) [Name of the invention]

Fluorine containing compounds

(57) [Summary]

[Structure]

Fluorine containing compounds having a structure, represented according to the described here below general formula

[1]

$$CH_2 = C(CH_2OCOR_1)COOR_2 \qquad (I)$$

(where in the formula, R1 and R2 each represent correspondingly a hydrocarbon radical, that can also be substituted by a fluorine atom, and also, at least one of the R1 and R2 radicals, represents a hydrocarbon radical that is substituted by at least 3 fluorine atoms).

[Results]

The fluorine containing compounds according to the present invention have high polymerizability properties and the polymer material obtained by the polymerization has high oxygen permeability properties, and the materials formed from it are especially useful for intraoculate lenses.

[Range of the claims of the invention]

[Claim 1]

Fluorine containing compounds having a structure, represented according to the described here below general formula

[1]

$$CH_2 = C(CH_2OCOR_1)COOR_2 \quad (I)$$

(where in the formula, R1 and R2 each represent correspondingly a hydrocarbon radical, that can also be substituted by a fluorine atom, and also, at least one of the R1 and R2 radicals, represents a hydrocarbon radical that is substituted by at least 3 fluorine atoms).

[Detailed explanation of the invention]

[0001]

[Technological sphere of application]

The present invention is an invention about novel fluorine containing compounds. Regarding the suggested according to the present invention fluorine containing compounds, by their polymerization fluorine containing polymer materials are obtained that have low refraction index, and excellent transparency properties, shape stability properties, staining resistance properties, chemical resistance properties, oxygen permeability properties etc.. And the above described polymer materials can be used as fiber treatment agents, paint materials, adhesion inhibiting agents, dental materials, optical fiber, resistors used in lithographic applications, low refractive index materials, high oxygen permeability formed materials, and especially they are very useful as materials for synthetic cornea materials like contact lenses, intraocular lenses.

[0002]

[Previous technology and problems solved by the present invention]

The highly fluorinated acrylic type polymer materials have a number of characteristic properties. For example, it is known that they have excellent solvent resistance properties, excellent chemical resistant properties, low surface energy, high lubricating properties, low refractive index, inflammability properties, excellent oxygen permeability properties. As one type of molded (formed) products that advantageously use the properties of these fluorinated type polymer materials, the used in optical applications, transparent materials, for example, intraocular lense, can be pointed out.

[0003]

In the past, intraocular lenses have been used, where the man component of the composition material used, has been polymethacrylate. This polymethacrylate material is a material that has important advantages having excellent transparency properties, optical functions, and excellent mechanical properties. However it has the problem that the oxygen permeability properties are poor. When contact lenses that are manufactured by using such material with poor oxygen permeability properties, is placed on the eye ball, the amount of the oxygen that is supplied becomes small, and when this is placed there for a long period of time, there are many cases when congestion, swelling etc., inflammation damage are incurred.

[0004]

In order to improve the oxygen permeability properties of the methacrylic acid ester type polymer material, the vinyl type diester monomer material, where it is possible to introduce in the molecule of the monomer a large amount of fluorine atoms and silicon atoms, has attracted attention. For example, contact lenses have been suggested, that are formed from a copolymer material, that is obtained from the following two monomer materials: (1) fluoroalkyl itaconate type monomer material or oligosiloxanyl itaconate monomer material, where in the molecule of the itaconic acid diester molecule fluorine atom or oligosiloxane bond, are introduced, and (2) methacrylic acid ester type monomer material (explained according to the disclosed in the descriptions of the Japanese Patent Application Number Showa 60-32033, Japanese Patent Application Number Showa 62-92914 and Japanese Patent Application Number Showa 63-210115).

[0005]

However, when these copolymer materials are compared to the used in the past polymethylmethacrylate (PMMA) etc., polymethacrylates, the oxygen permeability properties have been improved, however, it is still an insufficient improvement. And then, because of that, a polymer material with improved oxygen permeability properties, is still desirable.

[0006]

Also, as one type of the vinyl type ester monomer materials, dialkyl fumarate has been suggested. However, there is the problem that this material has poor polymerizability properties relative to the methacrylic acid ester monomer material and moreover, for example, even in the case when it has been successfully copolymerized, this obtained copolymer material has very poor brittle mechanical properties (explained according to the descriptions disclosed in the Japanese Patent Application Number Showa 62-99720 and Japanese Patent Application Number Showa 62-212618).

[0007]

The goal of the present invention is to suggest novel fluorine containing compounds with high polymerizability properties. And where also regarding the obtained by the polymerization fluorine containing polymer material, it is a material where the oxygen permeability properties, the transparency properties, the shape stability properties, the staining resistance properties and the durability properties are at a level that it is practically appropriate to be used as a high oxygen permeability material for intraocular lenses etc., and it is possible to mold materials with excellent oxygen permeability properties.

[0008]

[Measures in order to solve the problems]

The authors of the present invention have conducted rigorous research experiments in order to achieve this goal. And as a result from that they have observed that a specific alpha-azyloxymethylacrylate type compound, namely, fluorine containing compounds represented according to the described here below general formula (I) have excellent polymerizability properties both relative to itself (homopolymerization) and also excellent copolymerizability properties. And they have also observed that the molded materials formed from the polymer material obtained by the polymerization, used as intraocular lenses, have mechanical properties, thermal properties, transparency properties and stain resistance properties that allow for their practical use, and also have excellent oxygen permeability properties. The present invention, is an invention that has been achieved based on this new knowledge. And it is an invention that is obtained by suggesting fluorine containing compounds according to the described here below general formula (I).

[0009]

[2]

$$\begin{array}{l} \quad CH_2\,OCOR_1 \\ \quad\quad I \\ CH_2 = CCOOR_2 \end{array} \qquad (I)$$

(here below called fluorine containing compounds (I)).

[0011] ([0010] is missing ? - translator's note)

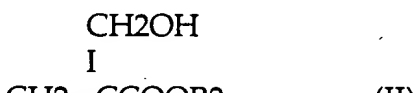
Moreover, the suggested according to the present invention fluorine containing compounds (I) have not been reported in the literature and they represent novel type compounds.

[0012]

The fluorine containing compounds (I) can be manufactured according to the well known methods from alpha-hydroxymethyl acrylate type compounds, represented according to the described here below general formula (II)

[0013]

[3]



(II)

[0014]

(R2 is the same as described here above) and a carboxylic acid represented according to the described here below general formula (III)

[0015]

[4]

(III)

[0016]

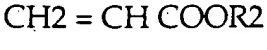
(where R1 is the same as in the above described), or its reactive derivative compound (for example, acid chloride etc., acid hallides).

[0017]

The represented according to the general formula (II) alpha-hydroxymethylacrylate type compound can be manufactured according to the well known method where to an acrylic acid ester represented according to the described here below general formula (IV)

[0018]

[5]



[0019]

(where R2 is the same as the described here above), under the presence of a catalyst, like for example 1, 4-diazabicyclo [2,2,2] octane, paraformaldehyde or formaline, are reacted. (For example, as described according to L. J. Mathias, Macromolecules, 20, 2326 (1987), M. Ueda et. al., J. Polym., Sci., Part A: Polym. Chem., 27, 751 (1989)).

[0020]

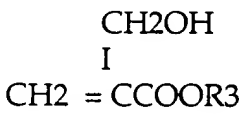
Also, regarding the alpha-hydroxymethylacrylate compound that is represented according to the general formula (II), it can be manufactured according to the well known methods, under the presence of an appropriate catalyst material, from propargyl alcohol, alcohol represented by the formula - R2OH (where R2 is according to the above described) and carbon monoxide (for example, as explained according to the described in the paper by Y. Watanabe and co-authors, J. Mol. Cat., 40, 295 (1987)).

[0021]

Especially, when instead of the used according to the above described method, alcohol represented by the formula R2OH (where R2 is according to the above described), an aliphatic alcohol is used that is represented according to the formula R3OH (where R3 represents an aliphatic hydrocarbon radical where the number of the carbon atoms is in the range of 1 ~ 12), it is possible to obtain a compound that is represented according to the described here below general formula (V)

[0022]

[6]



[0023]

Under the presence of an appropriate catalyst material, it is also possible to be manufactured by using the ester exchange reaction of the above described compound and the alcohol represented by the formula R2OH (where R2 represents the same as in the above described).

[0024]

According to the above described general formula (I), R1 represents a hydrocarbon radical, where it is a good option if it is substituted with fluorine atoms, and where preferably, the number of the carbon atoms is in the range of 1 ~ 12, and for example, it is possible to use the following here below radicals.

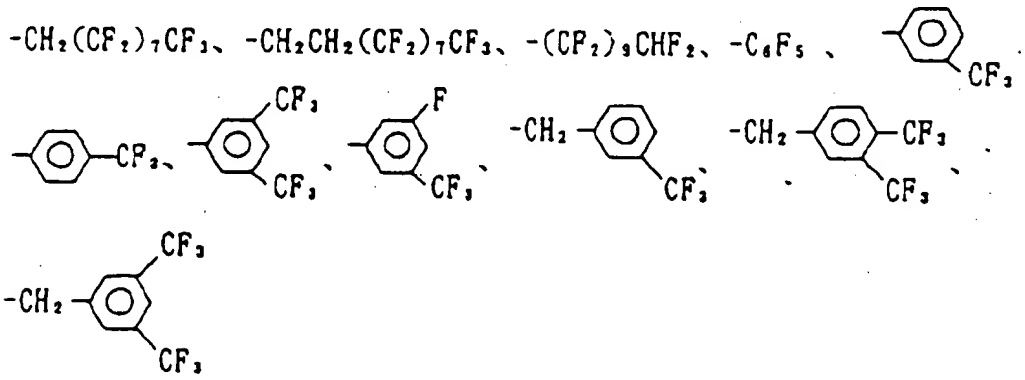
[0025]

And namely, alkyl radical, where it is also good if it is substituted by fluorine atoms, cycloalkyl radical, where it is also good if it is substituted by fluorine atoms, adamantan ring , where it is also good if it is substituted by fluorine atoms, aryl radical, where it is also good if it is substituted by fluorine atoms, aralkyl radical, where it is also good if it is substituted by fluorine atoms, can be used as the preferred materials. And in more details, it is possible to use the following here below radicals.

[0026]

[7]

$-CH_3$、$-CH_2CH_3$、$-CH(CH_3)_2$、$-(CH_2)_2CH_3$、$-C(CH_3)_3$、$-CH_2C(CH_3)_3$、$-(CH_2)_4CH_3$、$-C_6H_{11}$（以下シクロヘキサン環をC_6H_{11}で表す）[1]、$-C_{10}H_{15}$（以下アダマンタン環を$C_{10}H_{15}$で表す）[2]、$-C_6H_5$（以下フェニル基をC_6H_5で表す）[3]、$-CF_3$、$-CF_2CF_3$、$-CF_2CHF_2$、$-(CF_2)_2CF_3$、$-CHFCF_3$、$-CH_2CH_2CF_3$、$-CH_2CH(CH_3)CF_3$、$-(CF_2)_3CHF_2$、$-CH_2CH_2(CF_2)_2CF_3$、$-(CF_2)_4CHF_2$、$-(CF_2)_4CF_3$、$-CH_2(CF_2)_4CF_3$、$-CH_2CH_2(CF_2)_5CF_3$、$-(CF_2)_7CF_3$、$-(CF_2)_7CHF_2$、$-(CF_2)_5CF_3$、$-CH_2(CF_2)_7CF_3$、$-CH_2CH_2(CF_2)_7CF_3$、$-(CF_2)_9CHF_2$、$-C_6F_5$、



In the description of the formulae here above: 1. here below the cyclohexane ring is represented by C6H11), 2. here below, the adamantan ring is represented as C10 H15), 3. here below, the phenyl radical is represented by C6H5)

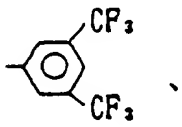
[0027]

Among these, the following here below are especially preferred.

[0028]

[8]

$CH(CH_3)_2$、$-C(CH_3)_3$、$-CH_2C(CH_3)_3$、$-C_6H_{11}$、$-C_{10}H_{15}$、
C_6H_5、$-CH_2CH_2(CF_2)_2CF_3$、$-(CF_2)_5CHF_2$、$-(CF_2)_5CF_3$、
$(CF_2)_6CF_3$、$-CH_2(CF_2)_6CF_3$、$-CH_2CH_2(CF_2)_6CF_3$、$-(CF_2)_7CF_3$、
$-(CF_2)_7CHF_2$、$-(CF_2)_8CF_3$、$-CH_2(CF_2)_7CF_3$、$-CH_2CH_2(CF_2)_7CF_3$、
$-(CF_2)_8CHF_2$、$-C_6F_5$、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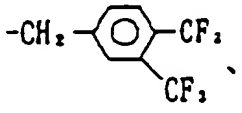
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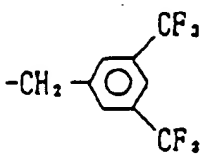


[0029]

Also, according to the above described general formula (I), R2 represents a hydrocarbon radical, where it is a good option if it is substituted with fluorine atoms, and where preferably, the number of the carbon atoms is in the range of 1 ~ 15, and for example, it is possible to use the following here below radicals.

[0030]

And namely, alkyl radical, where it is also good if it is substituted by fluorine atoms, cycloalkyl radical, where it is also good if it is substituted by fluorine atoms, adamantane ring , where it is also good if it is substituted by fluorine atoms can be used as the preferred materials. And in more details, it is possible to use the following here below radicals.

[0031]

[0031] $-CH_3$、$-CH_2CH_3$、$-(CH_2)_2CH_3$、$-CH(CH_3)_2$、$-(CH_2)_3CH_3$、$-CH_2C(CH_3)_3$、$-C_6H_{11}$、$-C_{10}H_{15}$、$-CH_2CF_3$、$-CH(CF_3)_2$、$-CH_2CH(CH_2C$ $H_3)(CH_2)_3CH_3$、$-CH_2CF_2CF_3$、$-CH_2(CF_2)_2CF_3$、$-CH_2(CF_2)_6CF_3$、$-CH_2CF_2CHF_2$、$-CH_2CF_2CHFCF_3$、$-CH_2(CF_2)_3CHF_2$、$-CH_2(CF_2)_5CHF_2$、$-CH_2(CF_2)_7CHF_2$、$-CH_2(CF_2)_8CHF_2$、$-CH_2CH_2CF_2CF_3$、$-CH_2CH_2(CF_2)_3CF_3$、$-CH_2CH_2(CF_2)_5CF_3$、$-CH_2CH_2(CF_2)_7CF_3$、$-CH_2CH_2(CF_2)_{11}CF_3$、$-CH_2CH_2(CF_2)_2CF(CF_3)_2$、$-CH_2CH_2(CF_2)_4CF(CF_3)_2$、$-CH_2CH_2(CF_2)_6CF(CF_3)_2$、$-CH_2CH_2(CF_2)_8CF(CF_3)_2$、$-(CH_2)_3CF_3$、$-(CH_2)_6CF_2CF_3$、$-(CH_2)_4(CF_2)_3CF$

7

, - $(CH_2)_6(CF_2)_3CF_3$, - $(CH_2)_6(CF_2)_7CF_3$, - $(CH_2)_6CF(CF_3)_2$, - $(CH_2)_6(CF_2)_2CF(CF_3)_2$, - $(CH_2)_6(CF_2)_4CF(CF_3)_2$, - $(CH_2)_6(CF_2)_6CF(CF_3)_2$

[0032]

Among those the following here below are especially preferred.

[0033]

8

[0033] $-CH(CH_3)_2$, $-CH_2C(CH_3)_3$, $-C_6H_{11}$, $-C_{10}H_{15}$, $-CH_2CF_3$, $-CH(CF_3)_2$, $-CH_2CH(CH_2CH_3)(CH_2)_3CH_3$, $-CH_2CF_2CF_3$, $-CH_2(CF_2)_2CF_3$, $-CH_2(CF_2)_6CF_3$, $-CH_2CF_2CHF_2$, $-CH_2CF_2CHFCF_3$, $-CH_2(CF_2)_3CHF_2$, $-CH_2(CF_2)_5CHF_2$, $-CH_2(CF_2)_7CHF_2$, $-CH_2(CF_2)_9CHF_2$, $-CH_2CH_2CF_2CF_3$, $-CH_2CH_2(CF_2)_3CF_3$, $-CH_2CH_2(CF_2)_5CF_3$, $-CH_2CH_2(CF_2)_7CF_3$, $-CH_2CH_2(CF_2)_9CF_3$, $-CH_2CH_2(CF_2)_{11}CF_3$, $-CH_2CH_2(CF_2)_2CF(CF_3)_2$, $-CH_2CH_2(CF_2)_4CF(CF_3)_2$, $-CH_2CH_2(CF_2)_6CF(CF_3)_2$, $-(CH_2)_3CF_3$, $-(CH_2)_6CF_2CF_3$, $-(CH_2)_6(CF_2)_3CF_3$, $-(CH_2)_6(CF_2)_5CF_3$, $-(CH_2)_6(CF_2)_7CF_3$, $-(CH_2)_6CF(CF_3)_2$, $-(CH_2)_6(CF_2)_2CF(CF_3)_2$, $-(CH_2)_6(CF_2)_4CF(CF_3)_2$, $-(CH_2)_6(CF_2)_6CF(CF_3)_2$

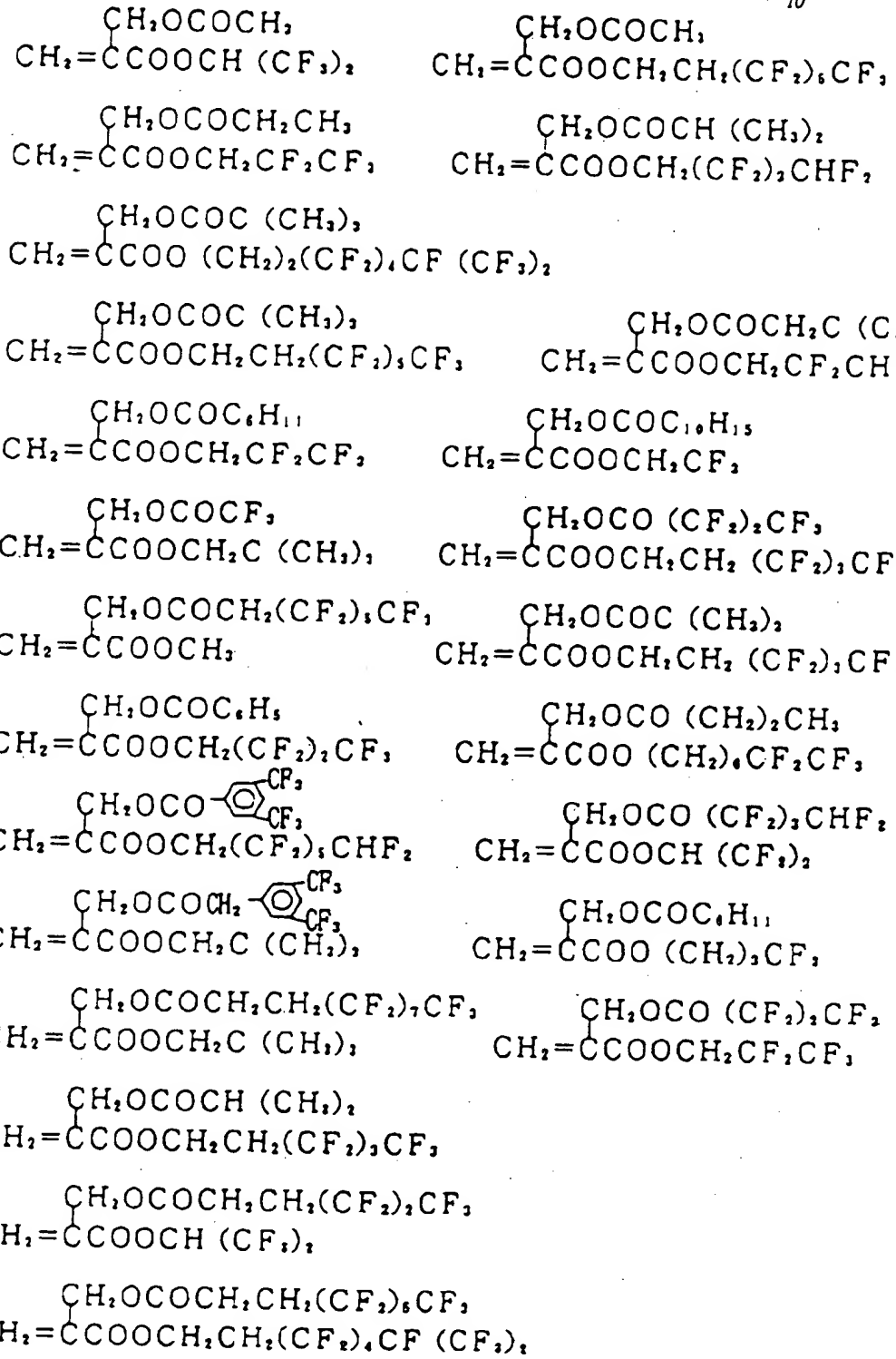
[0034]

Among the fluorine containing compounds (I), the preferred materials are listed according to the following here below.

[0035]

[9]

9　10



【0036】

【化10】

$$CH_2=\overset{CH_2OCOCH_2CH_2(CF_2)_4CF_3}{\underset{|}{C}}COOCH_2CH_2(CF_2)_4CF_3$$

$$CH_2=\overset{CH_2OCOCH_2C(CH_3)_3}{\underset{|}{C}}COOCH_2CH_2(CF_2)_4CF(CF_3)_2$$

$$CH_2=\overset{CH_2OCO(CF_2)_6CHF_2}{\underset{|}{C}}COOCH_2C(CH_3)_3$$

$$CH_2=\overset{CH_2OCOCH_2CH_2(CF_2)_4CF_3}{\underset{|}{C}}COOCH_2CH_2(CF_2)_4CF(CF_3)_2$$

$$CH_2=\overset{CH_2OCOCF_2CF_3}{\underset{|}{C}}COO(CH_2)_6(CF_2)_4CF_3$$

$$CH_2=\overset{CH_2OCOCH_2CH_2(CF_2)_4CF_3}{\underset{|}{C}}COOCH_2C(CH_3)_3$$

$$CH_2=\overset{CH_2OCO(CF_2)_6CF_3}{\underset{|}{C}}COOCH_2CH_2(CF_2)_4CF_3$$

$$CH_2=\overset{CH_2OCOCH_2CH_2(CF_2)_4CF_3}{\underset{|}{C}}COOCH_2CH_3$$

$$CH_2=\overset{CH_2OCO(CF_2)_6CHF_2}{\underset{|}{C}}COOCH_2CH_2(CF_2)_6CF_3$$

$$CH_2=\overset{CH_2OCOCH_2CH_2(CF_2)_4CF_3}{\underset{|}{C}}COOCH_2C(CH_3)_3$$

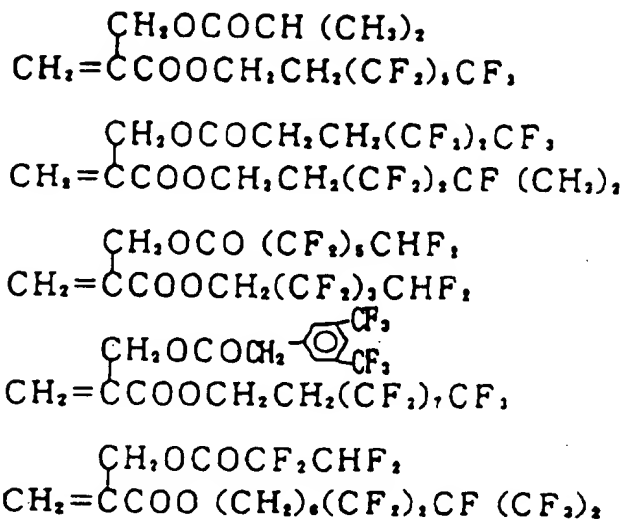
$$CH_2=\overset{CH_2OCOCF_2CHF_2}{\underset{|}{C}}COOCH_2CH_2(CF_2)_6CF(CF_3)_2$$

$$CH_2=\overset{CH_2OCOCH_2C(CH_3)_3}{\underset{|}{C}}COOCH_2CH_2(CF_2)_4CF_3$$

$$CH_2=\overset{CH_2OCOCH_3}{\underset{|}{C}}COOCH_2CH_2(CF_2)_6CF(CF_3)_2$$

【0037】

40　【化11】



【0038】フッ素含有化合物（I）のうち、特に好ましい化合物を次に示す。

【0039】
【化12】

$$CH_2=\overset{CH_2OCOC(CH_3)_3}{\overset{|}{C}}COO(CH_2)_2(CF_2)_4CF(CF_3)_2$$

$$CH_2=\overset{CH_2OCOC(CH_3)_3}{\overset{|}{C}}COOCH_2CH_2(CF_2)_5CF_3$$

$$CH_2=\overset{CH_2OCOC_6H_{11}}{\overset{|}{C}}COOCH_2CF_2CF_3$$

$$CH_2=\overset{CH_2OCO(CF_2)_5CHF_2}{\overset{|}{C}}COOCH_2CH_2(CF_2)_5CF_3$$

$$CH_2=\overset{CH_2OCO(CF_2)_7CF_3}{\overset{|}{C}}COOCH_2CH_2(CF_2)_3CF_3$$

$$CH_2=\overset{CH_2OCOC(CH_3)_3}{\overset{|}{C}}COOCH_2CH_2(CF_2)_3CF_3$$

$$CH_2=\overset{CH_2OCO-C_6H_3(CF_3)_2}{\overset{|}{C}}COOCH_2(CF_2)_5CHF_2$$

$$CH_2=\overset{CH_2OCO(CF_2)_5CHF_2}{\overset{|}{C}}COOCH_2C(CH_3)_3$$

$$CH_2=\overset{CH_2OCOCH_2-C_6H_3(CF_3)_2}{\overset{|}{C}}COOCH_2C(CH_3)_3$$

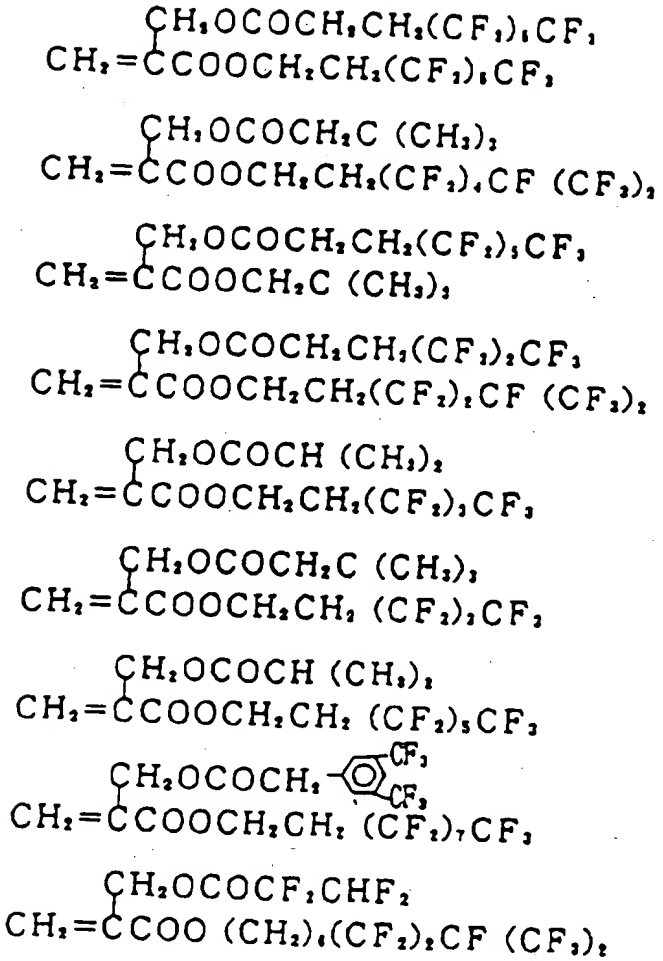
$$CH_2=\overset{CH_2OCOC_6H_{11}}{\overset{|}{C}}COO(CH_2)_3CF_3$$

$$CH_2=\overset{CH_2OCOCH_2CH_2(CF_2)_7CF_3}{\overset{|}{C}}COOCH_2C(CH_3)_3$$

$$CH_2=\overset{CH_2OCO(CF_2)_7CF_3}{\overset{|}{C}}COOCH_2CF_2CF_3$$

$$CH_2=\overset{CH_2OCOCH_2CH_2(CF_2)_5CF_3}{\overset{|}{C}}COOCH_2CH_2(CF_2)_4CF(CF_3)_2$$

【0040】　40　【化13】



(On separate pages.)

[0038]

Among the fluorine containing compounds (I), the especially preferred materials are listed according to the following here below.

(On separate pages.)

[0041]

The fluorine containing compounds (I), according to the present invention, demonstrate good polymerizability properties within themselves. And also, they show good copolymerizability properties with other polymerizable compounds, for example, radical polymerizable vinyl monomer, silicon containing vinyl monomer, crosslinkable multifunctional vinyl monomer etc., vinyl type monomers. Appropriate examples of the above described vinyl type monomer are described according to the following here below.

[0042]

Methyl (meth) acrylate, ethyl (meth) acrylate, isopropyl (meth) acrylate, t-butyl (meth) acrylate, neopentyl (meth) acrylate, cyclohexyl (meth) acrylate, benzyl (meth) acrylate, 2,2,2-trifluoroethyl (meth) acrylate, 1,1,2,2-tetrahydroperfluorooctyl (meth) acrylate, 1,1,2,2-tetrahydroperfluorodecyl (meth) acrylate, 2,2,2-trifluoro-1-trifluoromethylethyl (meth) acrylate, vinyl acetate, vinyl propionate, vinyl pibarinate, ethyl vinyl ether, n-butyl vinylether, styrene, p-methylstyrene, o-chlorostyrene, p-chlorostyrene, amide (meth) acrylate, 2-hydroxyethyl (meth)acrylate, N-vinyl pyrolidone, vinyl pyrdine, methacrylic acid, acryic acid, itaconic acid, etc., radical polymerization polymerizable vinyl type monomers; trimethyl silyl methyl (meth) acrylate, pentamethyl disiloxanylmethyl (meth) acrylate, methyl bis (trimethylsiloxy)silylmethyl (meth) acrylate, tris (trimethylsiloxy) silylmethyl (meth) acrylate, tris (pentamethyldisoloxanyloxy) silymethyl (meth) acrylate,trimethylsilyl ethyl (meth) acrylate, pentamethyldisoloxanyl ethyl (meth) acrylate, methyl bis (trimethylsiloxy) sylil ethyl (meth) acrylate, tris (trmethylsiloxy) silylethyl (meth) acrylate, tris (pentamethyldisiloxanyloxy) silylethyl (meth) acrylate, trmethylsilylpropyl (meth) acrylate, pentamethyldisiloxanyl (meth) acrylate, methylbis (trimethylsiloxy) silylpropyl (meth) acrylate, tris (trimethylsiloxy) silylpropyl (meth) acrylate, tris (pentamethyldisiloxanyloxy) silylpropyl (meth) acrylate,methylbis (trimethylsloxy)silylethylglycerol mono (meth) acrylate, tris (trimethylsiloxy) silylethyl glycerolmono (meth) acrylate, tris (pentamethyldisiloxanyloxy)

silylethyl glycerol mono (meth) acrylate, methyl bis (trimethylsiloxy) silyl propyl glycerol mono (meth) acrylate, tris (trimethylsiloxy) silylpropyl glycerol mono (meth) acrylate, tris (pentamethyldisiloxanyloxy) silylpropyl glycerol mono (meth) acrylate, dimethyl (triphenylsiloxy) silylpropyl (meth) acrylate, etc., silicon containing vinyl type monomers; divinyl benzene, vinyl (meth) acrylate, allyl (meth) acrylate, ethyleneglycol di (meth) acrylate, diethylene glycol di (meth) acrylate, triethyleneglycol di (meth) acrylate, dipropylene glycol di (meth) acrylate, diallylphtalate, diallylterephtalate, trimelitic acid triallylate, triallyl cyanurate etc., crosslinkable multifunctional vinyl type monomers etc., can be used. Regarding these vinyl monomers, they can be used individually or in a mixed combination, and it is possible to be copolymerized with the alpha-azyloxymethylacrylate type compound, according to the present invention.

[0043]

From the fluorine containing compounds (I) according to the present invention, or depending on the necessity, from a mixed material obtained from that material and other vinyl monomers, fluorine containing polymer materials can be obtained by a polymerization reaction according to the well known methods under the presence of polymerization initiation agent.

[0044]

As the polymerization initiation agents, that can be used, it is possible to select one type or two and more types from the group formed by the well known organic peroxide compounds and azo compounds etc.. As the organic peroxide compounds, for example, it is possible to use the following materials: acetyl peroxide, benzoyl peroxide, p-chlorobenzoyl peroxide, isobutyryl peroxide, bis (3, 5,5-trimethylhexanoyl) peroxide, t-butylhydroperoxide, cumenhydro peroxide, diisopropylbenzene peroxide, di-t-butyl peroxide, t-butylcumyl peroxide, dicumyl peroxide, 2, 5-dimethyl -2, 5-di (t-butyl peroxy) hexane, 1, 3-bis (t-butylperoxy) hexane, 1, 3-bis (t-butylperoxyisopropyl) benzene, 1,1 -dit-butylperoxy - 3,3,5-trimethylcyclohexane, 1,1-di t-butylperoxycyclohexane, 2,2 '-dit-butylperoxy butane, t-butylperoxy-2-ethylhexanoate, t-butylperoxypibarate, t-butylperoxydiisobutylate, t-butylperacetate, t-butylperbenzoate, t-butylperoxypropyl carbonate, diisopropylperoxy dicarbonate, peroxide lauroyl etc.. Also, as the azo type compounds, for example, azobisisobutylonitrile, azobiscyclohexanecarbonitrile, dimethylazobisisobutylate, azobisdimethylvaleronitrile etc., can be used.

[0045]

[Practical Examples]

Here below, the present invention will be explained in more detail by using practical examples and reference examples. However, the present invention is not limited by these practical examples.

[0046]

Practical Example 1

In a reaction vessel with a capacity of 2 liters, 500 grams of 1,1,2,2-tetrahydroperfluorooctyl acrylate, 95 grams of a 37 % formaldehyde water solution, and as a catalyst, 4.92 grams of 1, 4-diazabicyclo [2,2,2] octane, 600 ml of dioxane and as a polymerization inhibiting agent, 18.4 mg of p-methoxyphenol, were introduced. The stirring element was introduced and at a solution temperature of approximately 20oC, it was stirred by the stirrer for approximately 5 days. The solvent medium was removed by distillation under reduced pressure and after that to the remaining material methylene chloride was added and it was washed by using 10 % water solution of hydrochloric acid, and after that saturated water solution of sodium chloride and then with pure water. Next, this material was dried by using a dehydrating agent and then, by using an evaporator the solvent was removed. By the evaporation under reduced pressure, 180 grams of viscous liquid were obtained. Nuclear magnetic resonance spectrum was obtained as the material was dissolved in deuterated chloroform. From these results, it was confirmed that the above liquid material is 1, 1, 2, 2-tetrahydroperfluorooctyl (alpha-hydroxymethyl) acrylate.

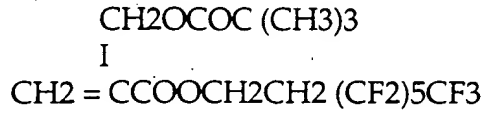
[0047]

After that, in a 1 liter triangular flask, 150 grams of 1, 1, 2, 2-tetrahydroperfluorooctyl (alpha-hydroxymethyl) acrylate, 26.5 grams of dried pyridine, 15.4 mg of p-methoxyphenol and approximately 300 ml of dried tetrahydrofuran, were introduced and under stirring in an ice bath, a solution of 40.4 g of pibaric acid chloride in approximately 150 ml of dried tetrahydrofuran, were added dropwise. After the completion of the dropwise addition, it was stirred at room temperature for approximately 20 hours and the esterification reaction was conducted. The separated salt was filtered and the solvent was removed and after that, to the remaining material methylene chloride was added and the material was washed by using 10 % water solution of hydrochloric acid, and after that saturated water solution of sodium chloride and then with pure water. Next, this material was dried by using a dehydrating agent and then, by using an evaporator the solvent was removed. the oily residue was distilled and by that a viscous liquid material was obtained (boiling point: 101.0 ~ 104.0oC/0.20 mmHg). The results from the nuclear magnetic resonance spectrum that was obtained as the material was dissolved in deuterated chloroform, are shown in Figure 1. From the

above described spectrum, it was confirmed that the above liquid material is a compound possessing the described here below structural formula.

[0048]

[14]



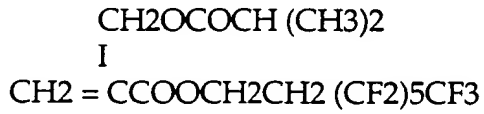
[0049]

Practical Example 2

Instead of the 40.4 grams of pibaric acid chloride used according to the procedures of the Practical Example 1, 35.7 grams of isoacetic acid chloride were used, and besides that everything else was conducted according to the same method as in the Practical Example 1 and an esterification reaction and an evaporation purification, were conducted. by that a viscous liquid material was obtained (boiling point: 105.0 ~ 107.0oC/0.15 mm Hg). The results from the nuclear magnetic resonance spectrum that was obtained as the material was dissolved in deuterated chloroform, are shown in Figure 2. From the above described spectrum, it was confirmed that the above liquid material is a compound possessing the described here below structural formula.

[0050]

[15]



[0051]

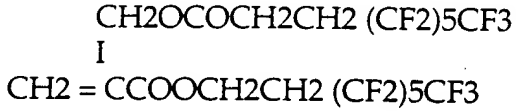
Practical Example 3

Instead of the 40.4 grams of pibaric acid chloride used according to the procedures of the Practical Example 1, 137.4 grams of 3- (perfluorohexyl) propyonyl chloride were used, and besides that everything else was conducted according to the same method as in the Practical Example 1 and an esterification reaction and a column purification were conducted. By that a

viscous liquid material was obtained . The results from the nuclear magnetic resonance spectrum that was obtained as the material was dissolved in deuterated chloroform, are shown in Figure 3. From the above described spectrum, it was confirmed that the above liquid material is a compound possessing the described here below structural formula.

[0052]

[16]



[0053]

Reference Example 1

To 10 grams of the obtained according to the Practical Example 1, 1,1,2,2-tetrahydroperfluorooctyl (alpha-pibaroyloxymethyl)acrylate, as a polymerization initiation agent, 4.9 mg of dimethylazobisisobutylate, is added and it is sufficiently stirred and mixed and in the polymerization tube, a freezing vacuum degassing is conducted and it is sealed. The polymerization tube is introduced into an isothermal vessel, and it is heated at a temperature of 60oC and a polymerization reaction is conducted. After the completion of the polymerization, the polymer material is extracted by resedimentation purification. The monomer material demonstrated excellent polymerizability properties and the polymer material yield was 78 %. After a vacuum drying, the polymer material was placed between parallel metal plates and under heating, it was brought to a molten state and by high pressure and cooling, a transparent film (thickness: 210 microns) was prepared. By using an oxygen permeability meter the oxygen permeability coefficient of this obtained experimental film at a temperature of 35oC, was measured. By that, it was concluded that this film had excellent oxygen permeability properties.

[0054]

Reference Example 2

To 5.0 grams of the obtained according to the Practical Example 1, 1,1,2,2-tetrahydroperfluorooctyl (alpha-pibaroyloxymethyl)acrylate, 2.0 g of tris (trimethylsiloxy)silylpropyl methacrylate are added, and as a polymerization initiation agent, 3.68 mg of dimethylazobisisobutylate, are added and it is sufficiently stirred and mixed and in the polymerization tube, a freezing vacuum degassing is conducted and it is sealed. The polymerization tube is

introduced into an isothermal vessel, and it is heated at a temperature of 60oC and a polymerization reaction is conducted. After the completion of the polymerization, the polymer material is extracted by resedimentation purification. The monomer material demonstrated excellent polymerizability properties and the polymer material yield was 95 %. After a vacuum drying, the polymer material was placed between parallel metal plates and under heating, it was brought to a molten state and by high pressure and cooling, a transparent film (thickness: 230 microns) was prepared. By using an oxygen permeability meter the oxygen permeability coefficient of this obtained experimental film at a temperature of 35oC, was measured. By that, it was concluded that this film had excellent oxygen permeability properties.

[0055]

[Results from the present invention]

The fluorine containing compounds (I) suggested according to the present invention have high polymerizability properties and the obtained by the polymerization polymer material has excellent oxygen permeability properties, and the materials formed from it are especially useful as intraocular lenses.

[Simple explanation of the figures]

[Figure 1]

It represents the Nuclear magnetic resonance spectrum of one compound included in the range of the present invention.

[Figure 2]

It represents the Nuclear magnetic resonance spectrum of one compound included in the range of the present invention.

[Figure 3]

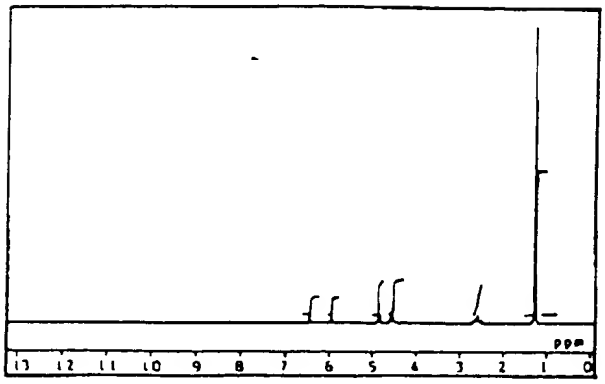
It represents the Nuclear magnetic resonance spectrum of one compound included in the range of the present invention.

Patent Assignee: Kuraray Company

Translated by Albena Blagev (6-7946)

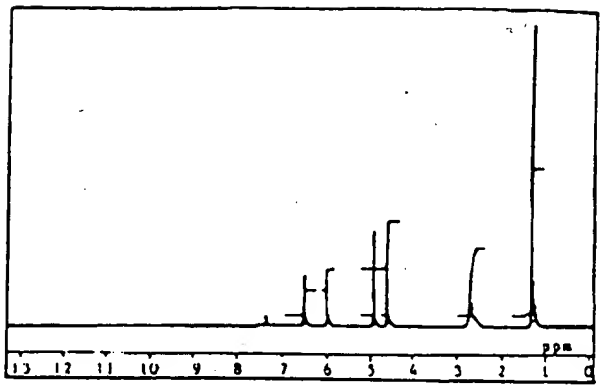
12/7/95

【図1】



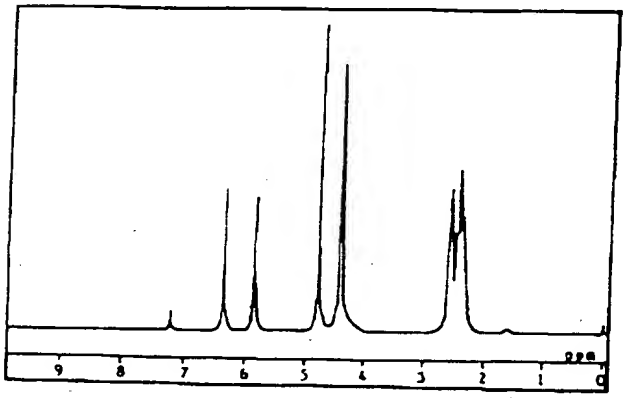
1. 30ppm $-CH_3$　　2. 60ppm $-CCH_2CF_3-$
4. 80ppm $-OCH_2C-$　　4. 85ppm $-C=CCH_2O-$
5. 85ppm $H\!>\!C=C<^{C-}_{COO-}$　　6. 45ppm $H\!>\!C=C<^{C-}_{COO-}$

【図2】



1. 30ppm $-CH_3$　　2. 60ppm $-CCH_2CF_3-$
2. 70ppm $-OCOCH-$　　4. 80ppm $-OCH_2C-$
4. 85ppm $-C=CCH_2O-$
5. 85ppm $H\!>\!C=C<^{C-}_{COO-}$　　6. 45ppm $H\!>\!C=C<^{C-}_{COO-}$

【図3】



2. 50ppm $-CCH_2CF_3-$　　2. 70ppm $-OCOCH_2C-$
4. 50ppm $-OCH_2C-$　　4. 90ppm $-C=CCH_2O-$
5. 95ppm $H\!>\!C=C<^{C-}_{COO-}$　　6. 45ppm $H\!>\!C=C<^{C-}_{COO-}$

フロントページの続き

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